Photodissociation of HN_3: direct formation of hydrogen atoms

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The formation of hydrogen atoms as primary products in the one-photon dissociation of HN_3 at 193 and 248 nm has been observed. The H atoms are detected by VUV spectroscopy using a frequency-tripled dye laser. The values for the quantum yield ϕ are $\phi(193\ \mathrm{nm})=0.15\pm0.02$ and $\phi(248\ \mathrm{nm})=0.24\pm0.05$. The photodissociation of H_2S has been used as reference system.

1. Introduction

The four-atomic hydrazoic acid is involved in different elementary chemical and photochemical processes which are currently being studied. The IR overtone excitation of HN_3 in the electronic ground state, $\tilde{X}\,^1A'$, leads to N_2 and NH fragments where the NH molecule will be formed either in the ground state, $X\,^3\Sigma^-$, or in the singlet state, $a\,^1\Delta$, depending on the photolysis energy [1]:

$$HN_3+h\nu\rightarrow N_2(X\,^1\Sigma_g^+)+NH(X\,^3\Sigma^-)\,, \qquad (1)$$

$$HN_3+h\nu\rightarrow N_2(X\,^1\Sigma_g^+)+NH(a\,^1\Delta)\,. \qquad (2)$$

By contrast, the UV photodissociation of HN_3 from the first electronic excited state, $\tilde{A}\,^1A''$, leads to NH products in the first singlet state [2–6], since the reaction path (1) is spin forbidden. Especially the observation of vector correlations [4] and interpretation of the behavior of the Λ doublets [5] have significantly improved the understanding of the dissociation dynamics of reactions (1) and (2). At a photolysis wavelength of 193 nm, the formation of small amounts of NH in several low-lying electronic states is observed [3]. At even higher dissociation energies in the VUV, a considerable amount of NH in electronically excited singlet states, especially in $c\,^1\Pi$, is formed [7].

While the reaction of hydrogen atoms with N_3 has been studied recently [8], there is no direct observation of generation of nascent hydrogen atoms in the UV dissociation of HN_3:

$$HN_3+h\nu\rightarrow H(^2S)+N_3(\tilde{X}\,^2\Pi)\,, \qquad (3)$$

$$\rightarrow H(^2S)+N(^4S)+N_2(X\,^1\Sigma_g^+) \qquad (4)$$

In a quantitative measurement of H_2 and N_2 as final products in the photodissociation of hydrazoic acid at 214 nm, Konar et al. did not exclude the formation of hydrogen atoms by reactions (3) and (4), because some of the observed H_2 was not scavengeable by i-C_4H_{10} [9].

The formation of N_3 after photolysis of HN_3 was observed in several experiments [10,11]. However, the azide radical is assumed to be generated in a secondary reaction

$$NH(^1\Delta)+HN_3\rightarrow NH_2+N_3\,. \qquad (5)$$

In their pioneering work, Rohrer and Stuhl determined the quantum yield of NH formation in the photodissociation of HN_3 at 193 nm [3]. Since significantly less than one NH radical is produced per absorbed photon, another reaction channel can be expected.

In this Letter, we wish to present quantitative results for the direct formation of hydrogen atoms in the one-photon dissociation of HN_3 at 193 and 248 nm.

2. Experimental

Pure hydrazoic acid was generated by heating NaN_3 in excess of stearic acid [4]. The photolysis light was supplied by an excimer laser (Lambda Physik, EMG 201) operating at 10 Hz either with ArF (193 nm) or with KrF (248 nm) as active laser medium. The pulse energy inside the reaction chamber was 0.5–1.0 mJ at a beam diameter of 4 mm. The hydrogen atoms were detected by excitation of the $^2P \leftarrow {}^2S$ transition and observation of the fluorescence light by a solar blind multiplier (EMR 542G-08-18). Lyman-α radiation was generated by frequency tripling of the light of a dye laser (Lambda Physik, Fl 2002E) which was pumped by a XeCl excimer laser (Lambda Physik, LPX 100). The delay time between photolysing and analysing laser beam was kept constant at 50 ns with a jitter of less than 3 ns. Tripling was performed by focusing the dye-laser beam into a 13 cm long cell filled with about 9 kPa Kr. A LiF lens collimated the 3ω beam. Pulse energy was in the order of 10^{10} photons at a calculated diameter of circa 2 mm. In order to minimize the detection of scattered light, a series of baffles was introduced into the paths of both beams which were arranged perpendicular to each other.

3. Results and discussion

The detected signal $S(\nu)$ at a photolysis intensity I_λ is given by

$$S(\nu) \approx [\phi(\text{H–N}_3)\, I_\lambda \sigma_\lambda(\text{HN}_3)\, p(\text{HN}_3)] \times [I_\alpha \sigma(\text{H})] , \qquad (6)$$

where $\phi(\text{H–N}_3)$ is the quantum efficiency of the processes (3) and (4), $\sigma_\lambda(\text{HN}_3)$ the absorption cross-section at the photolysis wavelength λ, $p(\text{HN}_3)$ the pressure of hydrazoic acid, I_α the intensity of Lyman-α radiation, and $\sigma(\text{H})$ the absorption cross-section of hydrogen at frequency ν. The expression in the first bracket is proportional to the amount of generated H atoms and the second term represents the probability of exciting those products.

The quantum yield $\phi(\text{H–N}_3)$ was normalized to the quantum yield of H_2S photodissociation, which is assumed to be unity [12]. The H signal after H_2S fragmentation at wavelength λ is given by the same expression (6), using the corresponding values for H_2S. Thus, any influence of detection geometry or saturation effects will be minimized. In several different experimental runs, the integrated line intensities $\int S(\nu)\,d\nu$ of HN_3 and H_2S were determined at both photolysis wavelengths. In each individual run, the pressure of hydrazoic acid and hydrogen sulfide were identical but were varied from one experiment to another. No influence of the photolysis laser energy on the quantum yield was observable.

Minor preabsorption of the laser beams before entering the observation region was considered in the calculation, but influenced the measured quantum yield by only a few percent. The detected signal $S(\nu)$ is not caused by the photolysing or by the analysing beam alone, and is only observed when the probe pulse is delayed relative to the dissociating laser pulse.

In principle, hydrogen may also be generated by secondary reactions. However, increasing the delay time (>1 μs) does not increase but rather decreases the H atom signal, because the fragments are ejected with high recoil velocities. Using the measured Doppler width $\Delta\nu_D$ of H atoms generated in the photodissociation of HN_3, we calculated a mean recoil velocity of $v_H(193\ \text{nm}) \approx 18500$ m/s and $v_H(248\ \text{nm}) \approx 11300$ m/s corresponding to a kinetic energy of the products of $E_{kin}(193\ \text{nm}) \approx 14600\ \text{cm}^{-1}$ and $E_{kin}(248\ \text{nm}) \approx 5400\ \text{cm}^{-1}$, respectively. In addition to these experiments with nascent H atoms, measurements were also carried out with He in excess (1 kPa) and at longer delay times (50 ns to 100 μs). The Doppler width of the hydrogen was strongly reduced, but the measured quantum yield did not change within the experimental error of a few percent.

The results are summarized in table 1. The main uncertainty in the determination of $\phi(\text{H–N}_3)$ are not

Table 1
Quantum yield of H formation in the photodissociation of HN_3. The absorption cross-sections σ are taken from the literature [7,13–16]

	193 nm		248 nm	
	σ (cm^2)	ϕ	σ (cm^2)	ϕ
H_2S	6.4×10^{-18}	1	2.8×10^{-20}	1
HN_3	2.4×10^{-18}	0.15 ± 0.02	5.6×10^{-20}	0.24 ± 0.05

fluctuations during the experiment, but the absorption cross-section of HN_3 and H_2S at the photolysis wavelength. Therefore, the values of $\sigma(HN_3)$ and $\sigma(H_2S)$ used are also included in table 1.

It is surprising that the quantum yield for low HN_3 excitation energies is slightly higher than at high photolysis energies. However, at 193 nm the $\tilde{A}\,^1A''$, $\tilde{B}\,^1A'$, and $\tilde{C}\,^1A''$ states of hydrazoic acid are excited, while at 248 nm the photon energy is only sufficient to reach the first electronic excited state, $\tilde{A}\,^1A''$ [4,17,18]. It should be mentioned that the uncertainty in the absorption cross-section of H_2S may also be responsible for the high value of ϕ at 248 nm. At this wavelength, the published values vary from 2.2×10^{-20} [15] to 3.4×10^{-20} cm^2 [16].

The available energy for the products is given by $E_a = h\nu + E_{int}(HN_3) - E_{diss}$. Unfortunately, a precise value of the bond dissociation energy, E_{diss}, for generating the products in their lowest quantum state is not known. However, most recently, Casassa et al. [1] determined the dissociation energy for the fragmentation of $HN_3(\tilde{X}\,^1A')$ into $N_2(^1\Sigma_g^+)$ and $NH(^1\Delta)$: $E_{diss} \approx 18750$ cm^{-1}. With the known thermodynamical data for $NH(^1\Delta) \rightarrow N(^4S) + H(^2S)$, $E_{diss} \approx 16020$ cm^{-1}, we obtain the dissociation energy of process (4), $E_{diss} \approx 34770$ cm^{-1}, corresponding to a threshold wavelength for the dissociation of cold HN_3 of $\lambda_0(HN_3 \rightarrow H+N+N_2) \approx 287.6$ nm. The heat of formation of N_3 is also not known accurately. A discussion of the N_3 bond dissociation energy is included in the paper of Alexander and Werner [19]. Newest measurements and theoretical calculations give a value of $E_{diss}(N_3 \rightarrow N_2+N) \approx 160$ cm^{-1} [19–21]. Therefore, the threshold wavelength for generation of hydrogen and the azide radical is $\lambda_0(HN_3 \rightarrow H+N_3) \approx 288.9$ nm. The available energy for $H+N_3$ at a photolysis wavelength of 193 and 248 nm is 17580 and 6090 cm^{-1}, respectively, using $E_{int}(HN_3) \approx 380$ cm^{-1} [4].

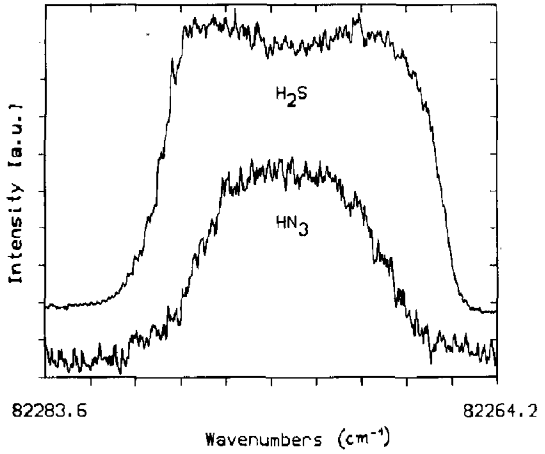

Fig. 1. Laser-induced fluorescence spectrum of hydrogen atoms generated in the photodissociation of HN_3 at 193 nm in comparison with H atoms from H_2S.

Since the reaction channels $H+N_3$ and $H+N+N_2$ are almost isoenergetic, from energetic reasons one cannot decide which fragmentation channel ((3) or (4)) is responsible for hydrogen production. However, the dissociation into $H(^2S)+N_3(^2\Pi)$ is spin-allowed, while the other fragmentation channel, $H(^2S)+N(^4S)+N_2(^1\Sigma)$, is spin-forbidden. Ab initio calculations by Meyer and Staemmler [17,18,22] for a change of the N_3–H distance of the $\tilde{A}\,^1A''$ state indicate only a small barrier of 0.29 eV at a distance of 127 pm. The other coordinates were kept constant at their equilibrium value. A change of this geometry will further strongly reduce the barrier height [22], and a fragmentation into H and N_3 becomes more likely. In that case, the N_3 product should exhibit a significant amount of internal excitation. The ab initio calculations also show a small barrier on the $\tilde{A}\,^1A''$ potential energy surface for the N_2–$NH(^1\Delta)$ separation [17,18], which is significantly lowered by changes of the N–N–N bending angles. This is verified by the experiment, where it was shown that in-plane and out-of-plane bending motions of the N_3 chain during the fragmentation lead to strongly internally excited products [4,23]. Therefore, we expect the generation of highly excited N_3 in the photodissociation of HN_3. Since the N_3–H bending-angle dependence on the upper potential is comparable to the ground state, $\tilde{X}\,^1A'$, we expect an azide product with low rotational excitation; however, due to the strong dependence of the upper potential on the two N–N–N bending angles, the N_3 fragment should be generated with a considerable amount of bending vibration (ν_2 mode).

We also observed the N_3 fragment by high-resolution laser-induced fluorescence (LIF) of the $\tilde{A}\,^2\Sigma_u 000 \leftarrow \tilde{X}\,^2\Pi_g 000$ and $\tilde{A}\,^2\Sigma_u 010 \leftarrow \tilde{X}\,^2\Pi_g 010$ transitions around 270 nm [24] after photolysis of HN_3 at 193 nm. However, at short delay times, the LIF signal decreases because N_3 is also generated according to reaction (5). Since the spectroscopy of high vibrationally excited states of N_3 is still unknown, we intend to study these states in order to elucidate the photodissociation dynamics of $HN_3(\tilde{A}\,^1A'')\rightarrow H(^2S)+N_3(^2\Pi_g)$.

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